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Magnetodeformation of ferrogels and ferroelastomers. Effect of microstructure of the particles' spatial disposition

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HIGHLIGHTS

- Magnetic field either elongates or contracts a ferrogel with single magnetizable particles.
- The type of deformation depends on the sample initial shape.
- The field elongates a ferrogel with chains independently on the sample shape.

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ABSTRACT

The work deals with the theoretical study of ferrogel/ferroelastomer deformations under the action of a homogeneous magnetic field. The compositions with linearly magnetizable non-Brownian particles are considered. Under the field action the ferrogel/ferroelastomer samples can either elongate or contract in the field direction. The type of deformation is determined by the sample shape and microstructure of the particles' spatial disposition. Two kinds of systems are studied. The first one is the composition with the particles homogeneously distributed, like in an ideal gas, in the polymer matrix. The second kind is the system of linear chain-like aggregates of densely situated particles. The results show that the particles' spatial disposition in the matrix is crucially important for the type of macroscopical deformation of the magnetopolymer compositions. The systems with the gas-like distribution of particles, depending on the sample shape, can either elongate or contract, whereas the chains stimulate the sample elongation.

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1. Introduction

Magnetic fluids present colloidal suspensions of nano- and micron-sized magnetic particles in liquid media. These systems attract considerable interest of investigators and engineers due to a rich set of physical properties valuable for many high technologies. An overview of works on synthesis, properties and applications of various magnetic fluids can be found in the book [1].

For the last few decades compositions of fine magnetic particles in polymer matrices have been synthesized and studied by many scientific teams. Combination of valuable properties of magnetic fluids with the properties of the polymer systems is very promising for many modern technologies [2–5]. The most frequently synthesized magnetopolymer compositions are so-called ferrogels and ferroelastomers. In the first systems the particles are embedded into gel matrices, in the second ones — into elastomers. The main difference between these systems lies in their mechanical properties — the gels are much softer than the elastomers.

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A homogeneous magnetic field can deform the magnetopolymers, either elongating or contracting them in the field direction. Deformation of the ferrogels and ferroelastomers under the action of an external magnetic field have been studied experimentally in Refs. [6–8], theoretically in Refs. [9–15], and by using computer simulations in Refs. [16–19].

One of the fundamental and most discussed problems of the science on magnetopolymer composites is a question about the type of their magnetodeformation — either the samples elongate or contract in the direction of the applied field. Results of laboratory experiments and computer simulations, known from literature, very often contradict each other. Thus, contraction of the samples has been detected in the works [7,12,13,16], whereas elongation — in Refs. [8,19]. An overview and analysis of internal mechanisms of the macroscopical deformations of these systems can be found in Ref. [20].

Theoretical analysis of Refs. [13,15] shows that the type of the magnetodeformation is determined by competition of two mechanisms. The first one is the change of the sample demagnetizing factor, as a consequence of the sample deformation. This factor stimulates elongation of the sample along the applied field. The second mechanism is the change of the sample magnetic susceptibility due to the change of the mutual disposition of the particles after the sample deformation. For single particles homogeneously distributed (like in a gas) in the matrix, the second mechanism stimulates contraction of the sample [13,15].

The work [13] deals with compositions of linearly magnetizable particles in a polymer matrix. This model is based on the estimates [21] of the ferrogel magnetic properties. However, in its turn, the estimates of Ref. [21] are based on the well known semi-empirical Lorentz approximation, developed for calculation of the effective susceptibility of compositions with magnetizable particles.

Although the Lorentz approach leads to quite acceptable estimates for the effective susceptibility, in the situation when the qualitative result (either elongation or contraction of the composition) is a consequence of competition between two different mechanisms, even a small inaccuracy of the semi-empirical approach can lead to qualitative mistakes. On the other hand magnetic particles in ferrogels and elastomers very often form linear chains and other heterogeneous structures [7,21–25]. The way of generalization of the Lorentz approach to these situations is not obvious. That is why development of mathematically regular methods of analysis of the magnetodeformation of the magnetopolymer compositions presents actual and important problems.

Deformations of ferrogels with single-domain ferromagnetic particles are considered in Ref. [15] on the basis of regular methods of statistical physics. However single-domain particles, as a rule, are very fine (about 10–20 nm in diameter) and magnetic interaction between them is weak. That is why mechanical effects, induced by the nano-particles, usually, are weak. These effects, produced by the magnetizable particles with a size about 100 nm–1 μm, as a rule, are significantly stronger than those produced by the single-domain particles.

From the theoretical point of view, the main difference between the compositions with the single-domain and magnetizable particles lies, first of all, in the fact that in the first systems absolute magnitudes of the particle magnetic moments are constant, whereas in the second systems the moment of a particle depends on the applied magnetic field and the field, created by the other particles of the composition. Secondly, the energy of magnetic interaction between the fine single-domain particles, usually, has the same order of magnitude as the thermal energy kT. In contrast, the energy of interaction between the multidomain magnetizable particles, as a rule, is significantly more than kT. That is why a microscopical description of these systems requires quite different theoretical approaches.

In this work we consider magnetodeformation of compositions of magnetizable spherical particles in a polymer matrix. Unlike Ref. [13], the presented approach is based on the regular method of reflections, which has been used successfully in hydromechanics of weakly and moderately concentrated suspensions [26,27]. Two types of these compositions are studied. The first one is a ferrogel/elastomer with homogeneously (like in an ideal gas) spatial distribution of the particles in the matrix. The second one is the system where the particles are united into linear chains. The chain-like structures very often appear in ferrogels under the action of a magnetic field applied before the matrix polymerization. Curing of the matrix fixes these structures. The chain formation changes significantly the mechanical, electrical and other properties of the compositions [7,25]. These transformations are valuable for many practical applications of the magnetic gels and elastomers [7,20]. It should be noted that the effect of the heterogeneous structures on deformation of the magnetopolymer compositions has not been considered theoretically, in spite of the fact that they have been often observed in experiments (see, for example, Refs. [21–25]).

Our goal is to determine the type (either elongation or contraction) of the magnetopolymer deformations under the action of the homogeneous external magnetic field $\mathbf{H}_0$. The regular method of reflections allows us to avoid artificial results, which are especially probable at the analysis of the systems with heterogeneous aggregates. It appears that analysis of infinitely small deformations is quite sufficient for determination of the type of the deformation. That is why only very small deformations of the samples will be considered. It will be supposed that the composites consist of identical spherical linearly magnetizable particles.

2. Macroscopical consideration

For maximal simplification of the mathematical part of the work, let us suppose that the sample presents an ellipsoid of revolution with the axes equal to $a \neq b = c$. The ellipsoidal shape provides homogeneity of the internal magnetic field $\mathbf{H}$ inside the sample and allows us to use the well-known explicit expressions [28] for the sample demagnetizing factor. That is very important for analytical study of the magnetomechanical effects.

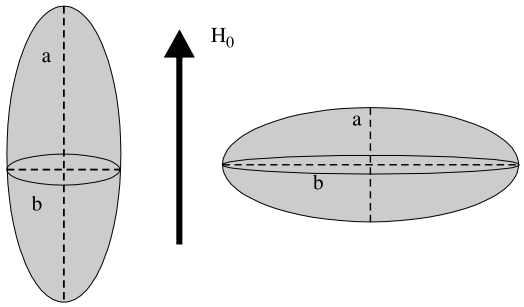

Fig. 1. Sketch of the initially prolate (left) and oblate (right) sample.

We suppose also that the external magnetic field $\mathbf{H}_0$ is aligned along the main axis a of the ellipsoid. This model situation is illustrated in Fig. 1. For simplicity we will assume that the polymer is incompressible. It should be noted that in many real situations the condition of the polymer matrix incompressibility is not fulfilled. However any small deformations can be presented as combinations of the change of the sample shape at the permanent volume and the change of its volume at the same shape. In the linear approximation these deformations can be considered separately. Here we will focus on the analysis of the change of the ferrogel shape. That is why we can consider these deformations at the invariable sample volume.

Let us denote the lengths of the axes a and b of the non-deformed sample as a_0 and b_0 respectively. We consider only small deformations of the sample and suppose that the axes of the deformed ellipsoid are

$$a = a_0\,(1 + 2\varepsilon)\,, \qquad b = b_0\,(1 - \varepsilon)\,, \quad \varepsilon \ll 1. \tag{1}$$

One can show easily that, in the linear approximation with respect to ε, relations (1) are in agreement with the condition of the sample incompressibility. The positive sign of ε corresponds to the elongation of the sample in the field direction, the negative one — to its contraction.

Free energy F of the deformed sample can be presented as a sum of the elastic part F_{el}, corresponding to the macroscopical deformation of the matrix, and the magnetic part F_m, which corresponds to the magnetic interaction of the particles with the applied field and with each other as well. The elastic term F_{el} is always positive and, for small deformations, $F_{el} \sim \varepsilon^2$. We will show below that the change of the magnetic free energy $\delta F_m \sim \varepsilon$. Thus when the strong inequality $\varepsilon \ll 1$ is fulfilled, the main contribution to the change of the total free energy F gives the magnetic term δF_m. The sign of this term determines the type of the sample deformation. Keeping in mind determination of the qualitative type of the deformation (not its amplitude), below we will consider only the change δF_m of the magnetic free energy F_m.

For maximal simplification of calculations let us suppose that the linear law of particle magnetization is fulfilled. For the particles on the basis of iron or its alloys usually this approximation is applicable for a field strength about 10 kA/m.

The free energy of a magnetizable ellipsoid in the external field H_0 in the Gauss system of units can be presented as [28]:

$$F_m = -\frac{1}{8\pi}\,\frac{\mu_e - 1}{1 + (\mu_e - 1)\,N}\,H_0^2. \tag{2}$$

Here, respectively, μ_e and N are the component of the tensor of the sample effective magnetic permeability and its demagnetizing factor in the direction of the field H_0 (i.e. in the direction of the axis a). For simplicity we suppose that the sample volume equals unity.

Change of the sample shape leads to change of its demagnetizing factor N as well as to the change of its effective permeability μ_e [28]. In the linear approximation with respect to ε the change of the magnetic free energy F_m can be calculated as:

$$\delta F_m = -\frac{1}{8\pi}\,\frac{H_0^2}{(1 + (\mu_e - 1)\,N)^2}\left[\delta\mu_e - (\mu_e - 1)^2\,\delta N\right]. \tag{3}$$

Here $\delta\mu_e$ and δN are changes, in the field direction, of μ_e and N due to the sample deformation. The general condition of the thermodynamic equilibrium (minimum of free energy) means that the real deformations must correspond to a decrease of F_m, i.e. to the inequality $\delta F_m < 0$.

Let us denote $s = b/a$. The case $s < 1$ corresponds to the prolate ellipsoid, the case $s > 1$ — to the oblate one. Taking into account (1), in the linear approximation in ε one can present the change of the demagnetizing factor as

$$\delta N = \frac{\partial N}{\partial s}\,\frac{\partial s}{\partial \varepsilon}\,\varepsilon = -3\,\frac{\partial N}{\partial s}\,s_0\varepsilon. \tag{4}$$

The derivate $\partial N/\partial s$ must be calculated for $s = s_0 = b_0/a_0$.

By using the well known formulas for the demagnetizing factor N (see, for example, Ref. [28]), one can present:

$$N = \begin{cases} \dfrac{s^2}{2\left(1-s^2\right)^{3/2}}\left[\ln\dfrac{1+\sqrt{1-s^2}}{1-\sqrt{1-s^2}} - 2\sqrt{1-s^2}\right], & s<1 \\ \dfrac{1+\sqrt{s^2-1}}{\left(s^2-1\right)^{3/2}}\left[\sqrt{s^2-1} - \operatorname{a\,tan}\sqrt{s^2-1}\right], & s>1. \end{cases} \tag{5}$$

Combining (4) and (5), one can easily calculate δN in (3).

We will calculate magnetic permeability μ_e as well as its change $\delta\mu_e$ separately for the cases of the homogeneous gas-like distribution of the particles and for the case when they form the linear chains.

3. Sample with homogeneously distributed particles

Let us consider a weakly concentrated composite assuming that the volume concentration φ of the magnetic particles is not more than several per cent. We suppose that the particles are homogeneously distributed, like in a gas of hard spheres, in the polymer matrix. The particles are identical linearly magnetizable spheres.

The effective magnetic permeability μ_e of a system with linearly magnetizable spheres can be presented in the following form (see, for example, Refs. [28,29]):

$$\mu_e = 1 + \left(\mu_p - 1\right)\varphi\frac{\langle h_p\rangle}{H}. \tag{6}$$

Here H is the macroscopical field inside the sample, h_p is the field inside an arbitrary "trial" particle, $\langle h_p\rangle$ is the field, averaged over positions of all other particles, and μ_p is the magnetic permeability of the particle material. The fact that the magnetic permeability of the polymer matrix equals unity is taken into account in (6).

When the volume concentration φ of the particles is small and any interactions between them can be neglected, the problem of the determination of h_p has the following strict solution [28,29]:

$$h_p^0 = \frac{3}{2+\mu_p}H. \tag{7}$$

Here and below the superscript 0 denotes the physical magnitudes, determined in the approximation of the non-interacting particles. Obviously in this approximation the equality $\langle h_p\rangle = h_p^0$ is held.

When magnetic interaction between particles is sufficient, the problem on determination of the field h_p does not have a strict solution. Examples of semi-empirical methods of calculation of $\langle h_p\rangle$ and, therefore, of μ_e one can find in Refs. [29,30].

In the case when the concentration φ is not high, the field h_p can be estimated in the pair approximation, taking into account interaction of two particles and neglecting any effect of the other ones on the local magnetic field around and inside the particles. In this case strict calculation of h_p requires solution of the well-known magnetostatic problem by using the bispherical coordinate system. It leads to cumbersome calculations and final results, whose generalization to the system with chains is rather impossible.

Here we use the regular method of reflections, justified when the mean distance between the particles is significantly more than the particle size. This condition is fulfilled when the concentration φ is small, i.e. under the same condition when the pair approximation is justified.

Detailed justification and examples of successful application of the method of reflection to the problems of hydromechanics of suspensions of the hard spheres can be found in Refs. [26,27]. It should be noted that the well known Batchelor formula [27] for the effective viscosity of suspensions of hard spheres, obtained in this approximation, leads to good agreement with experiments up to 10–15 per cent of the particles' volume concentration.

Let us consider two magnetizable particles, which we will mark by 1 and 2 (Fig. 2).

In the approximation of the non-interacting particles, magnetic moment m of each particle is [28]:

$$m^0 = \frac{3\left(\mu_p - 1\right)}{4\pi\left(2+\mu_p\right)}\mathrm{v}_p H. \tag{8}$$

Here v_p is volume of the particle, and $\mathbf{H}$ is the magnetic field, external with respect to the particles, i.e. the mean field inside the sample. Let us denote as r and θ the distance between the particle centers and the angle between the field $\mathbf{H}$ and radius-vector $\mathbf{r}$, connecting centers of the particles, respectively.

Magnetic moment m^0 of the first particle induces a magnetic field inside the second one. In the approximation of the dipole–dipole interaction, justified when the distance r between the particles is large as compared with the particle diameter, the induced field component in the direction of $\mathbf{H}$ is

$$m^0\frac{3\cos^2\theta - 1}{r^3}\frac{3}{2+\mu_p}.$$

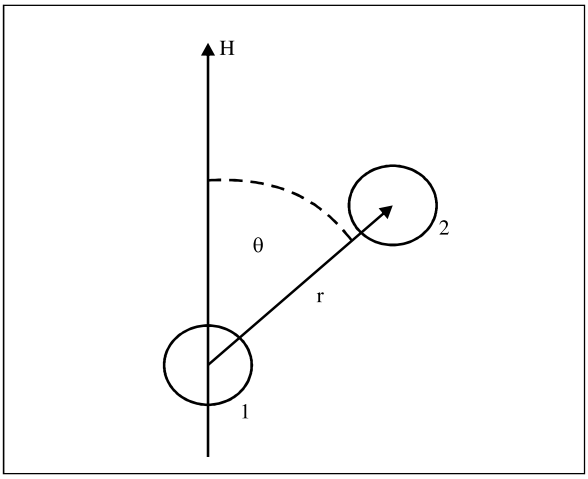

Fig. 2. Cluster of two interacting particles. Explanations are in the text.

Inside the second particle this field creates the moment

$$m^0 \frac{3\cos^2\theta - 1}{r^3} \frac{3\left(\mu_p - 1\right)}{4\pi\left(2 + \mu_p\right)} \mathrm{v}_p \tag{9}$$

$$\alpha = \frac{3}{4\pi}\beta, \qquad \beta = \frac{\mu_p - 1}{2 + \mu_p}.$$

Here β is the magnetic contrast factor of the particles.

Therefore, in the first approximation of the method of reflections, magnetic moment of the second particle can be estimated as:

$$m_2^1 = m^0 \left(1 + \alpha \mathrm{v}_p \frac{3\cos^2\theta - 1}{r^3}\right), \tag{10}$$

The subscripts 1, 2 here and below correspond to the numbers 1 or 2 of the particle (see Fig. 2); the superscripts mark the iteration of the reflection procedure.

The moment (10) of the second particle creates, inside the first particle, the field with the vertical (i.e. along the **H**) component

$$m_2^1 \frac{3\cos^2\theta - 1}{r^3} \frac{3}{2 + \mu_p}.$$

This field induces the following moment inside the first particle

$$m_2^1 \frac{3\cos^2\theta - 1}{r^3} \alpha \mathrm{v}_p. \tag{11}$$

Summing the moment (11) with the moment (8), taking into account Eq. (10), one can find the moment inside the first particle, corresponding to the second iteration of reflection:

$$m_1^2 = m^0 \left(1 + \alpha \mathrm{v}_p \frac{3\cos^2\theta - 1}{r^3} + \left(\alpha \mathrm{v}_p \frac{3\cos^2\theta - 1}{r^3}\right)^2\right). \tag{12}$$

Continuation of this procedure leads to the following expression for the moment m inside each of these particles

$$m = m^0 + m',$$

$$m' = m^0 \sum_{k=1}^{\infty} \left(\alpha \mathrm{v}_p \frac{3\cos^2\theta - 1}{r^3}\right)^k. \tag{13}$$

Here $m'(r, \theta)$ is the part of the magnetic moment of each particle, induced by the other one, situated in the point with the coordinates r, θ.

By using the general relations between magnetic field and moment inside a magnetizable particle, one can show easily that the field h_p inside each of the particles is

$$h_p(r,\theta) = h_p^0 + h_p', \qquad h_p' = h_p^0 \sum_{k=1}^{\infty} \left(\alpha \mathrm{v}_p \frac{3\cos^2\theta - 1}{r^3} \right)^k. \tag{14}$$

Let us discuss now the question on convergence of the power series (13) and (14). The maximal magnitude of the term αv_p corresponds to the asymptotic $\mu_p \to \infty$ and equal to $d^3/8$, where d is the diameter of the particle. The minimal distance r between the particle centers corresponds to the contact of the particles and equals the particle diameter d. Therefore the maximal magnitude of the term $\left(3\cos^2\theta - 1\right)/r^3$ is $2/d^3$. Thus the series ((13) and (14)) converge faster than the geometric progression with the denominator $\frac{1}{4}$.

The mean field $\langle h_p \rangle$ in (7) can be obtained by averaging of (14) over all physically possible positions of the second particle. It should be noted that in calculating the field and moment of a particle, induced by the other particle, we ignored the field and moment components in the directions, perpendicular to the field **H**, since the average magnitudes of these components equal zero.

Let us denote the pair function of the particles' spatial distribution as $g(\boldsymbol{r})$. For this distribution function we will use the normalization condition: $g \to 1$, when $r \to \infty$.

The mean magnitude of the field, induced in the first particle by the other ones, in the pair approximation is:

$$\langle h_p' \rangle = \frac{\varphi}{\mathrm{v_p}} \int h_p'(\mathbf{r}) g(\mathbf{r})\, \mathrm{d}\mathbf{r}. \tag{15}$$

Therefore:

$$\langle h_p \rangle = h_p^0 + \frac{\varphi}{\mathrm{v_p}} \int h_p'(\mathbf{r}) g(\mathbf{r})\, \mathrm{d}\mathbf{r}. \tag{16}$$

Substituting (16) into (6), we calculate the effective magnetic permeability μ_e of the composition.

The pair distribution function can be presented as:

$$g = g_0 + \delta g. \tag{17}$$

Here g_0 is the function g in the non deformed sample, and δg is the change of this function due to sample deformation.

In the linear approximation with respect to ε the following relation

$$\delta g = -\varepsilon r \left(3\cos^2\theta - 1\right) \frac{\mathrm{dg_0}}{\mathrm{d}r} \tag{18}$$

has been obtained in Ref. [21] from the general continuation equation for the function g.

Substituting Eq. (17) into (16) and, then, into (6), we get:

$$\mu_e = \mu_{e0} + \delta\mu_e \tag{19}$$

$$\mu_{e0} = 1 + \left(\mu_p - 1\right)\varphi \frac{\langle h_p \rangle_0}{H}, \qquad \delta\mu_e = \left(\mu_p - 1\right)\varphi \frac{\delta\langle h_p \rangle}{H}.$$

Here

$$\langle h_p \rangle_0 = h_p^0 + \frac{\varphi}{\mathrm{v_p}} \int h_p'(\mathbf{r}) g_0(\mathbf{r})\, \mathrm{d}\mathbf{r}. \tag{20}$$

$$\delta\langle h_p \rangle = \frac{\varphi}{\mathrm{v_p}} \int h_p'(\mathbf{r}) \delta g(\mathbf{r})\, \mathrm{d}\mathbf{r}.$$

The magnitude μ_{e0} presents effective magnetic permeability of the non-deformed sample, and $\delta\mu_e$ is the change of this permeability due to sample deformation. Calculations of effective dielectric permeability of a suspension of polarizable, gas-like distributed particles, by using the same approach as in (19), have been done in Ref. [31]. The calculated value of the permeability is quite close to that obtained in Ref. [32] on the basis of the solution of the two-particle problem by using the so-called method of twin spherical expansion. Because of mathematical identity of the problems of calculations of the magnetic and dielectric permeabilities, the results of Ref. [31] can be used for determination of μ_{e0}. The agreement between the permeabilities calculated in Refs. [31,32] shows that the method of reflections leads to quite reliable results.

We will show below that, calculating the change of the free energy δF_m in the framework of the pair approximation, in the square brackets (3) we must use the term $\mu_e - 1$, determined in the linear approximation with respect to the concentration φ. Thus in (3) we will use the approximation

$$\mu_e = 1 + 3\beta\varphi. \tag{21}$$

Now we are in a position to determine the change $\delta\mu_e$ of the magnetic susceptibility of the sample as a consequence of its deformation. For the systems with small particle concentration φ the distribution function g in the non-deformed sample

can be presented as:

$$g_0 = \begin{cases} 0, & r < d \\ 1, & r > d. \end{cases}$$

In this approximation $\frac{dg_0}{dr} = \delta(r-d)$, where $\delta(x)$ is the Dirac function.

Combining this relation with (18), we get

$$\int h'_p(\mathbf{r})\delta g \, d\mathbf{r} = -2\pi\varepsilon \int_0^{\pi} h'_p(\theta)\left(3\cos^2\theta - 1\right)\sin\theta \, d\theta. \tag{22}$$

Here $h'_p(\theta)$ is the magnitude of $h'_p(\mathbf{r})$ when $r = d$. Taking into account that the series (14) converges faster than the geometrical progression with the denominator $\frac{1}{4}$, in Eq. (22) we will neglect the third and further terms of (14). By using the first two terms of (14) in (22), substituting the result of integration into the third relation of (19), after simple calculations we get:

$$\delta\mu_e = -\varepsilon\varphi^2 (3\beta)^2 \left[\frac{4}{5} + \frac{2}{35}\beta\right]. \tag{23}$$

The first term (i.e. 4/5) of the last multiplier of (23) corresponds to the first term of the series (14), the second one — to the second term.

In the pair approximation the term $\delta\mu_e$ is proportional to φ^2. That is why in the square brackets of (3) we must calculate the term $\mu_e - 1$ in the linear approximation with respect to φ. Otherwise two terms in the brackets (3) will be calculated in different approximations with respect to φ.

Let us introduce the dimensionless parameter

$$q = -\left[3\beta\varphi\right]^{-2}\left[\delta\mu_e - (\mu_e - 1)^2 \delta N\right]. \tag{24}$$

Parameter q does not have a special physical meaning. It is just proportional to the ratio $\delta F_m/\varphi^2$ and, in the framework of the discussed approximation, does not depend either on H or on φ. When the strong inequality $\mu_p \gg 1$ is held (which is typical for real ferrogels and elastomers), parameter q is practically independent on the particle permeability μ_p. That is why q depends only on the sample aspect ratio s; this is convenient for analysis of variation of the sign of δF_m with s.

First, let us consider the spherical sample ($a_0 = b_0$). Taking into account the well known relations [28] for the demagnetizing factor N of the almost spherical ellipsoids, after simple calculations in the linear approximation in ε we get

$$\delta N = -\frac{4}{5}\varepsilon. \tag{25}$$

Substituting Eqs. (21), (23) and (25) into (24), for the initially spherical sample we get:

$$q = \varepsilon\left(\frac{2}{35}\beta\right). \tag{26}$$

When $\varepsilon > 0$ (i.e. the sphere elongates under the field action) parameter q, and thus the change δF_m of the sample free energy, is positive; when $\varepsilon < 0$ (the sphere contracts) q and δF_m are negative.

This means that contraction of the sphere in the field direction is thermodynamically profitable. It should be noted that the results of Ref. [13], based on the semi-empirical Lorentz model, indicate that the spherical sample cannot be deformed by the field — change of the magnetic free energy of a sphere in Ref. [13] equals zero. One can easily show that neglecting, in the second square brackets of (23), the term $\frac{2}{35}\beta$ (i.e. restricting ourselves by the first iteration of the reflections), we will get the result $q = 0$. This means that in the approximation of the first reflection, like in the model [13], the sphere does not experience magnetodeformation. The usage of the second iteration of the method of reflections allows us to predict contraction of the sphere.

Results of calculations of the parameter $q' = q/\varepsilon$ as a function of the form-factor s_0 of the non-deformed sample are shown in Fig. 3. When $q' > 0$ contraction of the sample in the field direction is thermodynamically profitable, otherwise the elongation is profitable. The results show that initially spherical ($s_0 = 1$), strongly oblate ($s_0 \gg 1$) and prolate ($s_0 < 1$) samples will contract in the field direction. There is an "island" of intermediate magnitudes of the shape parameter s_0, corresponding to the elongation of the initially moderately oblate spheroid. The conclusion on the "island of elongation" of the magnitudes of the shape parameter has been done in Refs. [13,15]. Of course, the values of boundaries of the "island" in the model [13] and here, obtained by using the regular method of reflection, are different.

The reason of the appearance of the "island of elongation" is as follows. One can show, by using Eqs. (4) and (5), that the ratio $\delta N/\varepsilon$ is negative and non-monotonic, with minimum, depending on the shape-factor s_0 of the non-deformed sample. This ratio comes to zero when s_0 tends both to zero and to infinity. At the same time, the term $\delta\mu_e/\varepsilon$ does not depend on s_0. Our analysis shows that for the case of the single particles the ratio $\delta\mu_e/\varepsilon$ is negative and its absolute value is less than the maximum of the absolute value of the term $(\mu_e - 1)^2 \delta N/\varepsilon$. Thus the term q', which is proportional to $-\left(\delta\mu_e - (\mu_e - 1)^2 \delta N\right)/\varepsilon$, equals zero in two points of s_0, negative between them and positive outside them (see Fig. 3).

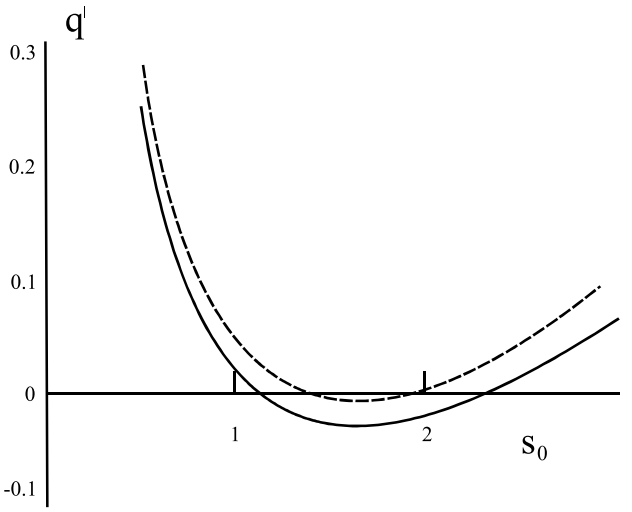

Fig. 3. The dimensionless parameter $q' = q/\varepsilon$ vs. the shape-factor s_0 of the non-deformed sample. The solid line corresponds to $\mu_p = 2$; the dashed one — to $\mu_p = 20$.

The negative sign of q' corresponds to elongation of the sample, the positive sign — to its contraction. Physically this means that when $q' < 0$, the elongating effect of the demagnetizing field dominates over the contracting effect of the change of the sample magnetic susceptibility. When $q' > 0$ the situation is opposite — the contracting effect of the susceptibility dominates over the elongating effect of the demagnetizing field.

In the next section we will show, that for the ferrogel with relatively short chains, the term $\delta\mu_e/\varepsilon$ is always positive. This means that q' is negative for all s_0. That corresponds to elongation of the ellipsoidal sample with any initial shape, since both the effect of the demagnetizing field and the effect of the change of the sample susceptibility stimulate elongation of the sample.

4. Ferrogel with parallel chains

Let us suppose now that the polymer matrix has been cured in the presence of an external homogeneous magnetic field (the field of polymerization). It is well known that in a liquid matrix under the field action magnetizable particles can form chains and other heterogeneous aggregates, parallel to the field direction [7,21–24]. We will consider the situation when only chains appear in this composite.

The field of polymerization, as well as the field $\mathbf{H}_0$, which induces deformation of the sample, can have arbitrary orientations with respect to the sample axes. Analysis of the general case leads to cumbersome calculations and final results. Here we restrict ourselves to the simplest case when the directions of both fields coincide with the main axis of the sample, i.e. with the direction of the axis a in Fig. 1. In this case all chains are parallel to the field of deformation $\mathbf{H}_0$.

After the matrix curing, the size of the formed chains depends on the strength of the field of polymerization, competition between the rates of the chain formation and the matrix polymerization, as well as on other factors including the particles' space disposition before the moment when the field was switched on. That is why determination of the chain size distribution requires a special analysis for every concrete situation and cannot be performed in the general case.

Here, for simplicity, we will suppose that all chains consist of the identical number n of particles. We will suppose also that the length of the chain nd is much less than the sizes a and b of the sample. The considered situation is illustrated in Fig. 4. Next, we will suppose that the magnetic forces between the nearest particles in each chain are much stronger than the elastic forces in the matrix, which tend to deform the chain due to the macroscopical deformation of the sample. In other words, we will suppose that the chains do not experience deformation and have the same structure of the straight linear aggregates of closely spaced particles as in the non-deformed ferrogel.

It should be noted that in many cases the lengths of the chains in ferrogels and elastomers are nearly equal to the sample thickness; often they percolate the samples [7]. This situation does not correspond to our consideration and requires a special study.

Following the general thermodynamic relation (3), in order to determine the type of sample deformation, one needs to estimate its effective permeability μ_e and change $\delta\mu_e$ of this permeability. To this end we need to estimate magnetization M of the sample. By definition

$$\mu_e - 1 = 4\pi \frac{M}{H}. \tag{27}$$

Here H is the macroscopical field inside the sample.

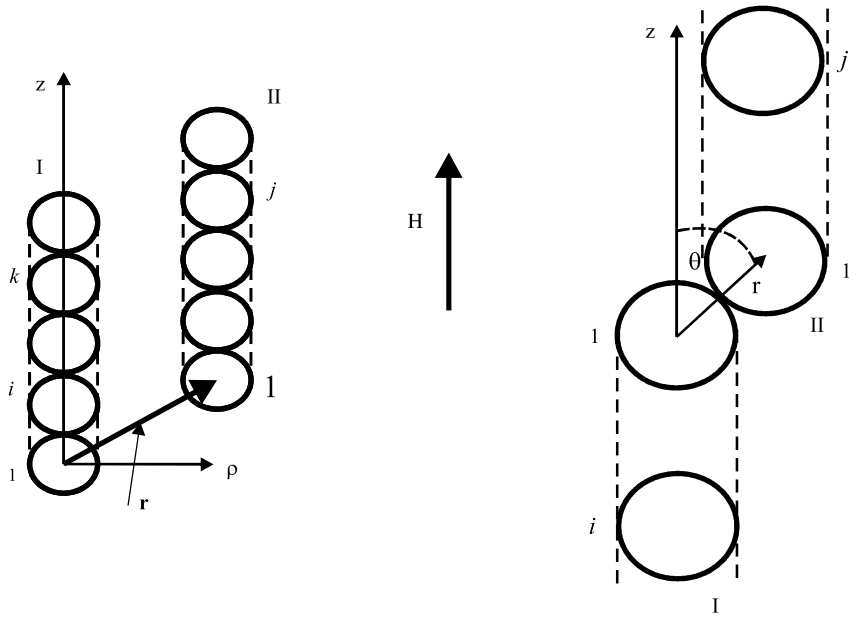

Fig. 4. Sketch of the chains in the composition. Explanations are in the text.

Since $M = \varphi m/v_p$ (where m is the mean magnetic moment of a particle in the system) in order to determine the permeability μ_e we need to determine the moment m.

Similar to the case of the gas-like spatial distribution of the particles, we will suppose that the particle volume concentration φ is small. It will allow us to consider interaction between the chains by using the regular pair approximation. On the other hand, obviously, magnetic interaction between the closely situated particles in a chain is significantly stronger than this interaction between the particles which belong to the different chains. Thus, in the first approximation, we can determine μ_e by estimating the particle magnetic moment m taking into account interaction of the particles in one chain, and neglecting interaction between particles in the different chains.

Strict calculation of the magnetic moment of a particle in the chain requires solution of a magnetostatic problem, both inside and outside the chain, taking into account standard boundary conditions on the chain surface. However this problem cannot be solved strictly because of the complicated shape of the chain. In order to achieve physically reasonable estimates, here we will use a general idea of the mean-field approximation.

It should be noted that the magnetic moment of a particle in the chain depends on its position in this cluster. We will suppose that all particles in the chain have identical moment m, which is equal to the mean moment of the particles in this aggregate.

Let us consider a chain, consisting of the contacting magnetic particles (see Fig. 4). In the framework of the discussed approximation, the field h_i, created by all particles of the chain inside the particles with the number i, can be estimated as

$$h_i = \frac{m}{d^3} 2f_i, \qquad f_i = \sum_{\substack{k=1,\\ k\neq i}}^{n} \frac{1}{|k-i|^3}. \tag{28}$$

The i-th particle can be considered as situated in the magnetic field $H_i = H + h_i$. Magnetic moment m_i, induced by the total field H_i inside the i-th particle, can be estimated as [28]

$$m_i = \alpha H_i = \alpha \left(H + \frac{m}{d^3} 2f_i\right) \tag{29}$$

$$\alpha = \frac{3}{4\pi} \beta \mathrm{v}_p.$$

Taking into account that for all situations, presenting an interest, the inequality $\mu_p \gg 1$ is held, we can use the estimate $\alpha = d^3/8$.

By definition the average magnetic moment of a particle in the chain is

$$m = \frac{1}{n} \sum_{i=1}^{n} m_i.$$

By averaging both sides of (29) over the number i, after simple transformations we get

$$m = \alpha H \frac{1}{1 - G(n)}, \qquad G(n) = \frac{2\alpha}{nd^3} \sum_{i=1}^{n} f_i. \tag{30}$$

Parameter G can be approximated by the formula

$$G = 0.593 \frac{n-1}{n}. \tag{31}$$

Simple calculations show that the maximal uncertainty of this approximation is about several per cent.

Combining Eqs. (30) and (31) with (27), we get an estimate for the magnetic permeability μ_e of the composition in the approximation of the non-interacting chains.

Now we are in a position to estimate the effect of the composition deformation on its permeability, i.e. to estimate the term $\delta\mu_e$ in (3). Let us denote by $W(\mathbf{r})$ the energy of magnetic interaction between two chains, shown in Fig. 4. We will mark these chains by I and II. Let the radius-vector $\mathbf{r}$, like in the left part of Fig. 4, link centers of the lowest particles of these chains. Taking into account that the number of chains per unit volume of the system is $\varphi/(v_p n)$, one can present the mean energy w of the chain's interaction per unit volume of the system as:

$$w = \frac{1}{2} \left(\frac{\varphi}{v_p n} \right)^2 \int W(\mathbf{r}) g(\mathbf{r})\, \mathrm{d}\mathbf{r}. \tag{32}$$

Here $g(\mathbf{r})$ is the pair distribution function of the chains with the same normalization condition $g \to 1$ when $r \to \infty$ as in the previous part. The relation (32) corresponds to the approximation of the pair interaction between the chains.

We can present again the distribution function g in the form (17). The change δg of this function, which takes place due to the sample deformation, can be found from the following equation [21]

$$\delta g = -\mathrm{div}(g_0 \mathbf{u}) = -\left(g_0 \mathrm{div}\mathbf{u} + (\mathbf{u} \cdot \nabla) g_0\right). \tag{33}$$

Here $\mathbf{u}$ is the vector of displacement of the medium, and g_0 is the function of mutual spatial distribution of the chains in the non -deformed sample. For the incompressible media $\mathrm{div}\mathbf{u} = 0$, thus Eq. (33) can be rewritten as:

$$\delta g = -(\mathbf{u} \cdot \nabla) g_0. \tag{34}$$

For the system of single spherical particles, which undergoes deformation (1), solution of Eq. (34) is given in (18).

Deformation of the sample leads to the change δg of the distribution function g. In its turn that leads to the change of the sample magnetic energy:

$$\delta w = \frac{1}{2} \left(\frac{\varphi}{v_p n} \right)^2 \int W(\mathbf{r}) \delta g(\mathbf{r})\, \mathrm{d}\mathbf{r} = -\frac{1}{2} \left(\frac{\varphi}{v_p n} \right)^2 \int W(\mathbf{r}) (\mathbf{u} \cdot \nabla) g_0\, \mathrm{d}\mathbf{r}. \tag{35}$$

The function g_0 equals zero when the chains interpenetrate and equals unity for all other mutual positions of the chains. For maximal simplification of calculation of the integral (35), let us model the n-particle chain by the spherocylinder whose diameter and length of the cylindrical part equal the particle diameter d and $d(n-1)$ respectively. These spherocylinders are illustrated in Fig. 4 by the dashed lines. In this case ∇g_0 is proportional to $\delta(\mathbf{r} - \mathbf{r}_s)$, where $\delta(x)$ is the delta-function, and $\mathbf{r}_s$ is the radius-vector, corresponding to the boundary of the region of the spherocylinders intersection. One can show easily that the surface, corresponding to $\mathbf{r}_s$, presents a spherocylinder with diameter $2d$; the length of the cylindrical part equals $d(n-1)$.

Neglecting the effect of the interchain interaction on magnetic moments of the particles in the chains, we can present the energy W of two chains' interaction as:

$$W(\mathbf{r}) = \frac{m^2}{d^3} \sum_{i,j=1}^{n} \omega(i, j, z', \rho'), \tag{36}$$

$$\omega(i, j, z', \rho') = -\frac{2\left(i - j + z'\right)^2 - \rho'^2}{\left[(i - j + z')^2 + \rho'^2\right]^{5/2}}, \quad z' = \frac{z}{d}, \ \rho' = \frac{\rho}{d}.$$

Here i and j are the numbers of particles in chains I and II in Fig. 4, z and ρ are cylindrical coordinates of the center of the lowest particle of chain 2, and $m^2\omega(i, j, z', \rho')/d^3$ is the energy of the dipole–dipole interaction between the i-th particle in the first chain and the j-th particle in the second one, when the dimensionless coordinates of the lowest particle of the second chain are z', ρ'.

Let us present the integral in (35) as

$$\int W(\mathbf{r}) (\mathbf{u} \cdot \nabla) g_0\, \mathrm{d}\mathbf{r} = m^2 \varepsilon J, \quad J = J_1 + J_2.$$

Here J_1 corresponds to integration over the cylindrical side of the spherocylinder excluded for the second chain (the surface of the excluded spherocylinder corresponds to the vector $\mathbf{r}_s$), J_2 — over the semispheres of this spherocylinder.

In a Cartesian coordinate system with the origin in the center of the lowest particle of chain I in Fig. 4, the components of the vector **u** are:

$$u_z = \varepsilon z, \qquad u_x = -\frac{1}{2}\varepsilon x, \qquad u_y = -\frac{1}{2}\varepsilon y.$$

Here the axis Oz, like in Fig. 4, is aligned along the direction of the internal field **H**.

In the cylindrical coordinate system, shown in the left part of Fig. 4, the non-zero components of this vector are:

$$u_z = \varepsilon z, \qquad u_\rho = -\frac{\varepsilon}{2}\rho. \tag{37}$$

Combining Eqs. (36) and (37), we can write down the integral J_1 in the following form

$$J_1 = -\frac{2\pi}{\varepsilon d}\int_{-(n-1)}^{n-1}\sum_{i,j=1}^{n}\omega(i,j,z',\rho')u_\rho\,\big|_{\rho=d}\;\mathrm{d}z' = 2\pi\int_{-(n-1)}^{n-1}\sum_{i,j=1}^{n}\omega(i,j,z',1)\,\mathrm{d}z'. \tag{38}$$

Here we take into account that the first integral in (38) must be calculated over the cylindrical part of the surface $\mathbf{r}_s$, i.e. at $\rho = d$. The last integral in (38) can easily be calculated numerically.

In order to calculate J_2, for convenience, we will use the spherical coordinate system, shown in the right part of Fig. 4 with the radius r and polar angle θ. In this system the radial component of the vector **u** is:

$$u_r = \frac{1}{2}\varepsilon r\left(3\cos^2\theta - 1\right).$$

The integral J_2 reads

$$\begin{aligned} J_2 &= -\frac{4\pi}{\varepsilon d}\int_0^{\pi/2}\sum_{i,j=1}^{n}\frac{2\left(i+j-2+r'\cos\theta\right)^2 - r'^2\sin^2\theta}{\left[(i+j-2+r'\cos\theta)^2 + r'^2\sin^2\theta\right]}u_r\,|_{r=d}\,\sin\theta\,\mathrm{d}\theta \\ &= -2\pi\int_0^{\pi/2}\sum_{i,j=1}^{n}\frac{2\,(i+j-2+\cos\theta)^2 - \sin^2\theta}{\left[(i+j-2+\cos\theta)^2 + \sin^2\theta\right]}\left(3\cos^2\theta - 1\right)\sin\theta\,\mathrm{d}\theta, \quad r' = r/d. \end{aligned} \tag{39}$$

We take into account here that the first integral in (39) must be calculated over the semispheres of the spherocylinder of the chain intersection (i.e. at $r = d$) and that the spherocylinder has two semispheres.

On the other hand, the change δw of the magnetic free energy can be presented as:

$$\delta w = -\frac{1}{8\pi}\delta\mu_e H^2. \tag{40}$$

It should be noted that δw is the change of the sample magnetic free energy only due to the change of the chains' mutual disposition as a consequence of the sample deformation. The effect of variation of the sample demagnetizing factor N is not taken into account here.

Combining (35) and (40), we get:

$$\delta\mu_e = 4\pi\frac{m^2}{H^2}\left(\frac{\varphi}{\mathrm{v_p}n}\right)^2\varepsilon J. \tag{41}$$

Both integrals J_1 and J_2 have been calculated numerically. The result of calculations of the dimensionless parameter J as a function of the number n of the particles in the chain is presented in Fig. 5.

This plot shows that for single particles ($n = 1$) the inequality $\delta\mu_e/\varepsilon < 0$ is held; for the systems with chains ($n \geq 2$) the ratio $\delta\mu_e/\varepsilon$ is positive. This means that elongation ($\varepsilon > 0$) of the sample with the single particles decreases its magnetic susceptibility; for the sample with chains this elongation leads to an increase of the susceptibility. It should be noted that this conclusion is on account of the chain magnetic interaction; it does not depend on the way of estimation of the particle magnetic moment m in the non-interacting chains.

One can show that for the single particles the estimate (41) of the susceptibility coincides with the estimate (23), corresponding to the first iteration of the method of reflections (i.e. only with the term 4/5 in the second square brackets of (23)).

Let us return now to relation (3). Since the ratio $\delta N/\varepsilon$ is negative (see Ref. (4)), the positive sign of the ratio $\delta\mu_e/\varepsilon$ (positive sign of J) means that for any initial shape of the sample its elongation ($\varepsilon > 0$) leads to a decrease of its magnetic free energy (i.e. to the inequality $\delta F_m < 0$). In other words, for the sample with the chains, both factors — change of the susceptibility μ_e as well as change of the demagnetizing factor N — stimulate elongation of the sample in the applied field direction. This conclusion coincides with the result of analysis of the effect of the chains on the type of ferrogel magnetodeformation, obtained in Ref. [20] by using computer simulations of a ferrogel.

It should be noted that this conclusion is made only for the case when the length of the chains is much less than the size of the sample. The elongation effect is induced by a change of mutual disposition of the chains and, therefore, by a change of energy of their magnetic interaction as a consequence of the sample deformation.

If the chains are long and percolate the sample, variation of their mutual disposition is rather impossible. In this case small contraction of the sample can take place because of a reduction of ultra-thin gaps between the neighboring particles in the chains [7]. However this case requires a special theoretical study.

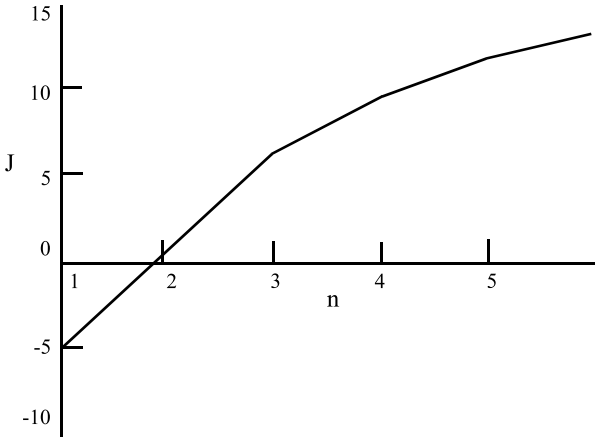

Fig. 5. Dimensionless parameter J vs. number n of particles in the chain.

5. Conclusion

Deformation of a ferrogel (ferroelastomer) with magnetizable colloidal particles under the action of a homogeneous magnetic field is considered theoretically. The results, based on the regular method of reflections, demonstrate that the sample with the single particles either elongates or contracts in the field direction, depending on the sample initial shape. Earlier similar conclusions have been made in Ref. [13] on the basis of a semi-empirical approach. Unlike Ref. [13] our results, based on the regular method of reflections, show that the spherical sample must contract in the direction of the field.

Appearance of the chains, parallel to the field of deformation, induces elongation of the sample, independently of its initial shape. We have supposed that the length of the chains is much less than the size of the sample and that the particles are closely spaced in the chains. Elongation of the samples takes place due to change, at the sample deformation, of the chain mutual disposition and, as a consequence, a change of the energy of their magnetic interaction.

If the chains percolate the sample, variation of their mutual disposition is impossible and the sample will rather contract [7] due to a decrease of ultra-thin gaps between the particles in the chain. Of course, this contraction must be very small. It should be noted that contraction of ferrogels with chains has been detected in the computer simulations [19]. However in these simulations the thickness of the interparticle gap was about the particle diameter. The chains like that can hardly appear in real ferrogels and elastomers.

Experimentally the effect of the chains on the ferrogel magnetodeformation has not been specially studied. However in experiments, where the chains of the densely situated particles took place, only elongation of the samples has been detected [16,22]. At the same time computer simulations of Ref. [20] demonstrate that the chain-like aggregates of closely situated particles stimulate elongation of the ferrogels in the field direction. Therefore the results of experiments [16,22] and computer simulations [16,20,22] are in agreement with the conclusion of the presented model.

Acknowledgments

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